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Thermal Shrinkage of Polypropylene Fibers in Several Solvents by Partial Melting of Crystalline Regions

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Thermal shrinkage of polypropylene fiber in several solvents was studied on the basis of Flory's theory of melting in polymer-diluent system. Difference between the Gibbs free energy in crystalline regions and that in amorphous regions, and the polymer fraction v_2' in amorphous regions were estimated from theoretical expression derived for the relative shrinkage $vs.$ temperature relation in polymer-diluent system.

INTRODUCTION

As reported in the previous papers,²⁻⁵⁾ it has been shown experimentally that the thermal shrinkage of fibrous polymers along the fiber axis may be mainly governed by the partial melting²⁻⁴⁾ of crystalline regions and the decrease in number of pseudo cross-links⁵⁾ in amorphous regions. Some experiments on the thermal shrinkage in the absence of diluent have been performed for some polymers.

In this paper, we investigate the thermal shrinkage of polypropylene fibers in various solvents and discuss the experimental results on the basis of the theory¹⁾ of melting for polymer-diluent system.

THEORETICAL TREATMENT

It was already shown in the previous paper²⁾ that the change in Gibbs free energy $[(h_u - Ts_u) - (h_x - Ts_x) + f(a-1)]$ per structural unit accompanying disappearance of crystalline regions in the mixture of polymer and solvent was given by

$$\frac{(h_u - Ts_u) - (h_x - Ts_x) + f(a-1)}{kT} = \frac{(z/z_s)(1-v_2) + (v_2/x)}{1-v_2(1-\lambda)} + \frac{1}{x-\xi+1} - \chi_1 \left\{ \frac{1-v_2}{1-v_2(1-\lambda)} \right\}^2 + \frac{\nu}{xN_A} \left\{ \frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right\} \quad (1)$$

h_u : heat of fusion per structural unit.

s_u : entropy of fusion per structural unit.

h_x : heat of transition per structural unit due to pseudo cross-links in amorphous regions.

s_x : entropy of transition per structural unit due to pseudo cross-links in amorphous regions.

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- f : force.
 a : drawing ratio.
 k : Boltzmann's constant.
 z : number of segments per structural unit.
 z_s : ratio of molar volume of solvent to volume of a segment.
 v_2 : volume fraction of polymer.
 x : total number of structural units in a polymer chain.
 λ : amorphous fraction.
 χ_1 : interaction free energy parameter.
 N_A : Avogadro's number.
 ν : number of pseudo cross-links per unit volume.
 v_2' : polymer fraction in amorphous regions.

$$v_2' = v_2 / (1 - v_2 + v_2')$$

Alternatively,

$$v_2 = v_2' / \{v_2' + (1 - v_2')\lambda\} \quad (2)$$

and

$$\frac{1}{1 - v_2 + v_2\lambda} = \frac{v_2'}{v_2\lambda} = \frac{v_2' + (1 - v_2')\lambda}{\lambda} \quad (3)$$

Therefore, when $z = z_s$, substitution of eqs. (2) and (3) in eq. (1) leads to

$$\begin{aligned} \frac{(h_u - Ts_u) - (h_x - Ts_x) + f(a-1)}{kT} &= \frac{v_2'}{x\lambda} + (1 - v_2') + \frac{1}{x - \xi + 1} \\ &\quad - \chi_1(1 - v_2')^2 + \frac{\nu}{xN_A} \left\{ \frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right\} \end{aligned} \quad (4)$$

Whereas, the relative shrinkage S is represented by²⁾

$$S = (L_c - L_a)\lambda / L_c \quad (5)$$

where, L_c and L_a are the length of sample in totally crystalline and amorphous state, respectively. Substituting eq. (5) in eq. (4), we obtain the following relation between the relative shrinkage and temperature.

$$\begin{aligned} \frac{1}{S} &= \frac{xL_c}{(L_c - L_a)v_2'k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(a-1) \} \frac{1}{T} \\ &\quad - \frac{xL_c}{(L_c - L_a)v_2'} \left[(1 - v_2') + \frac{1}{x - \xi + 1} - \chi_1(1 - v_2')^2 \right. \\ &\quad \left. + \frac{\nu}{xN_A} \left\{ \frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right\} \right] \end{aligned} \quad (6)$$

When $\chi_1 = 0$, eq. (6) is written as

$$\begin{aligned} \frac{1}{S} &= \frac{xL_c}{(L_c - L_a)v_2'k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(a-1) \} \frac{1}{T} \\ &\quad - \frac{xL_c}{(L_c - L_a)v_2'} \left[(1 - v_2') + \frac{1}{x - \xi + 1} + \frac{\nu}{xN_A} \left\{ \frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right\} \right] \end{aligned} \quad (7)$$

and under the conditions, $\chi_1 = 0$ and $v_2' = 1$, eq. (7) is further reduced to

$$\begin{aligned} \frac{1}{S} &= \frac{xL_c}{(L_c - L_a)k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(a-1) \} \frac{1}{T} \\ &\quad - \frac{xL_c}{(L_c - L_a)} \frac{1}{x - \xi + 1} \end{aligned} \quad (8)$$

EXPERIMENTAL

Sample

Polypropylene mono-filament (375 d) of the birefringence $\Delta n=0.0339$ and the density at 23°C $\rho=0.8845$ was used in this work. The degree of polymerization x of this sample was estimated, from the intrinsic viscosity in decalin at 135°C according to the equation⁶ $[\eta]=1.10 \times 10^{-4} M_w^{0.80}$, as $x=4283$.

Measurement of Thermal Shrinkage

The thermal shrinkage of this sample was measured, by suspending a weight of 0.787 mg/d, in several solvents: toluene, *p*-xylene, styrene, *n*-octane, cyclohexanone, *n*-pentanol, and two Θ -solvents, dibenzyl ether and benzyl propionate. The change of the sample length was detected by a displacement meter and recorded on a X-Y recorder.

For polypropylene fiber used here, a value of 4% is expected for the relative shrinkage during the fiber manufacturing process.²⁾ Therefore, the correct value of S was obtained by adding 4% to the relative shrinkage calculated by using the length (observed value) of the original fiber at room temperature.

RESULTS AND DISCUSSION

Figure 1 and Fig. 2 show the relation between the relative shrinkage and the absolute temperature for the polypropylene fiber in solvents and in air. With respect to Fig. 1, the reciprocal of the relative shrinkage of this fiber in solvents may be plotted linearly against the reciprocal of the absolute temperature above ca. 75°C, except the cases in cyclohexanone, *n*-pentanol and air, for which curves are represented by a set of two straight lines. On the other hand, from Fig. 2 relating to two Θ -solvents, dibenzyl ether and benzyl propionate, it is pointed out that, above 50°C, each curve is represented by two straight lines intersecting at 82°C.

Straight line portion in the figures is represented by

$$\frac{1}{S} = A \frac{1}{T} - C, \quad (A \text{ and } C \text{ are constant}) \quad (9)$$

The constants A and C are, respectively, given by eqs. (10) and (11).

$$A = \frac{xL_c}{(L_c - L_a)v_2'k} \{ (h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1) \} \quad (10)$$

$$C = \frac{xL_c}{(L_c - L_a)v_2'} \left[(1 - v_2') + \frac{1}{x - \xi + 1} - \chi_1(1 - v_2')^2 + \frac{\nu}{xN_A} \left\{ \frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right\} \right] \quad (11)$$

When $\alpha \cong 1$ and $(h_u - h_x)/(s_u - s_x) = T_m (= \text{constant})$, eq. (10) is reduced to

$$\frac{1}{T} - \frac{1}{T_m} = \frac{A}{h_u - h_x} \frac{(L_c - L_a)v_2'k}{xL_c} \frac{1}{T} \quad (12)$$

Whereas, when x is very large, C in eq. (11) is written as

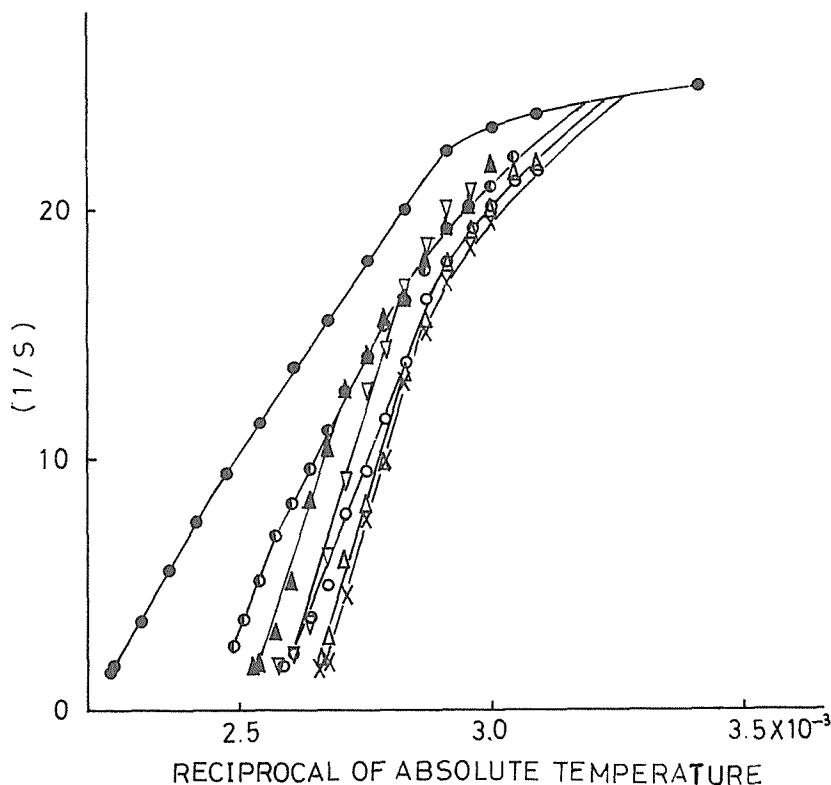


Fig. 1. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal absolute temperature $1/T$ for polypropylene fiber in several solvents.

● : air, × : *p*-xylene, △ : toluene, ○ : styrene,
 ▽ : *n*-octane, ▲ : cyclohexanone, ● : *n*-pentanol.

$$C = \frac{xL_c}{(L_c - L_a)v_2'} \{ (1 - v_2') - \chi_1(1 - v_2')^2 \} \quad (13)$$

where, $[(1 - v_2') - \chi_1(1 - v_2')^2]$ is generally represented⁷⁾ by

$$(1 - v_2') - \chi_1(1 - v_2')^2 = \frac{\Delta G_0}{kT} \quad (14)$$

in which ΔG_0 is the difference between the Gibbs free energy of crystalline regions and that of amorphous regions when x is very large. Therefore,

$$C = \frac{xL_c}{(L_c - L_a)v_2'} \frac{\Delta G_0}{kT} \quad (15)$$

and, further, from eqs. (10) and (15), the ratio of A to C is given by the following equation.

$$\frac{A}{C} = T \frac{\Delta G}{\Delta G_0}, \quad (16)$$

where, $\Delta G = (h_u - Ts_u) - (h_x - Ts_x) + f(a - 1)$.

On the other hand, the polymer fraction v_2' in the amorphous regions is obtained from eq. (11). If x is very large, then for $\chi_1 \neq 0$,

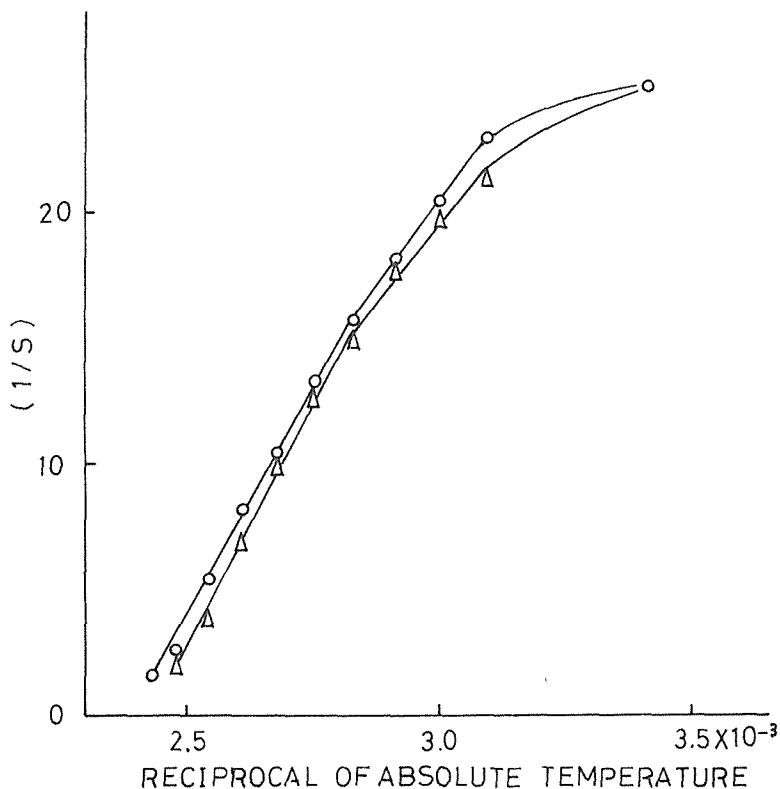


Fig. 2. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal absolute temperature $1/T$ for polypropylene fiber in dibenzyl ether (\circ) and benzyl propionate (\triangle).

$$v_2' = 1 - \frac{\left\{1 + \frac{C(L_c - L_a)}{xL_c}\right\} - \sqrt{\left\{1 + \frac{C(L_c - L_a)}{xL_c}\right\}^2 - 4 \frac{\chi_1 C(L_c - L_a)}{xL_c}}}{2\chi_1} \quad (17)$$

and for $\chi_1 = 0$,

$$v_2' = \frac{1}{1 + \{C(L_c - L_a)/xL_c\}} \quad (18)$$

In Table 1, numerical values of $N_A \Delta G$ and v_2' calculated for non-theta solvents assuming $\chi_1 = 0$, $\chi_1 = 0.5$, and $\chi_1 = 1.0$ were listed. As seen in Table 1, change in v_2' and $N_A \Delta G$ accompanied by the change in χ_1 from 0 to 1 was very small, notwithstanding these values may be slightly increased with increasing temperature, because χ_1 is a function of the temperature. In Table 1, also shown are the values of solubility parameter δ_s [$\delta_s = (\text{cohesive energy density})^{1/2}$] of solvents. With respect to dibenzyl ether and benzyl propionate, the entropy parameter ψ_1 and the theta temperature Θ are known as⁸⁾

$\psi_1 = 1.58$, $\Theta = 459.6^\circ\text{K}$ for dibenzyl ether

$\psi_1 = 1.37$, $\Theta = 430.5^\circ\text{K}$ for benzyl propionate.

Thus we can estimate the parameter χ_1 as a function of temperature from

$$\chi_1 = 0.5 + \chi_1 - \psi_1 \quad (19)$$

$$\chi_1 = \psi_1 \Theta / T \quad (20)$$

Table 1. $N_A\Delta G$ and v_2' for Polypropylene Fiber in Several Solvents.

Solvent	Temp. Range (°C)	z_1	δ_s (cal/cm ³) ^{1/2}	v_2'	$N_A\Delta G$ (cal/mol)
(Air)	70-135	—	—	1	9.186
	135-172	—	—	1	10.803
<i>n</i> -Octane	75-115*	0	7.80	0.9768	18.122
	75-115*	0.5		0.9762	18.117
	75-115*	1.0		0.9759	18.112
<i>p</i> -Xylene	75-103*	0	8.81	0.9744	19.180
	75-103*	0.5		0.9741	19.173
	75-103*	1.0		0.9737	19.166
Toluene	75-105*	0	8.94	0.9755	18.488
	75-105*	0.5		0.9752	18.482
	75-105*	1.0		0.9749	18.477
Styrene	75-118*	0	9.20	0.9815	14.351
	75-118*	0.5		0.9813	14.348
	75-118*	1.0		0.9811	14.346
Cyclohexanone	80- 95	0	9.92	0.9869	10.823
	80- 95	0.5		0.9868	10.822
	80- 95	1.0		0.9868	10.821
	95-122*	0		0.9778	17.486
	95-122*	0.5		0.9777	17.484
	95-122*	1.0		0.9773	17.478
<i>n</i> -Pentanol	80-115	0	10.55	0.9869	10.824
	80-115	0.5		0.9868	10.822
	80-115	1.0		0.9868	10.821
	115-128	0		0.9823	14.363
	115-128	0.5		0.9821	14.360
	115-128	1.0		0.9820	14.359

* denotes the melting temperature of polypropylene in solvent.

In Table 2, $N_A\Delta G$ and v_2' for theta-solvent systems were listed as a function of temperature. Figure 3 illustrate the change of $N_A\Delta G$ or v_2' with δ_s . It should be noted that the maximum point in $N_A\Delta G$ vs. δ_s curve and the minimum point in v_2' vs. δ_s curve appear at a δ_s value approximately corresponds to that, 8.20 (cal/cm³)^{1/2}, of polypropylene,⁹⁾ and moreover, the polymer fraction v_2' in amorphous regions is considerably large. The temperature dependences of v_2' and $N_A\Delta G$ for dibenzyl ether and benzyl propionate were represented in Figs. 4-7. From these Figs., it is pointed out that v_2' and $N_A\Delta G$ are changed abruptly at 82°C, *i.e.*, the former decreases and the latter increases with increasing temperature.

Thermal Shrinkage of Polypropylene Fibers

Table 2. $N_A\Delta G$ and v_2' vs. Temperature for Polypropylene Fiber in Theta Solvents.

Solvent	Dibenzyl ether			Benzyl propionate		
L_a/L_c	0.371			0.474		
Temp. (°C)	χ_1	v_2'	$N_A\Delta G$ (cal./mol.)	χ_1	v_2'	$N_A\Delta G$ (cal./mol.)
50	1.168	0.9913	7.669	0.956	0.9932	6.059
60	1.101	0.9913	7.669	0.901	0.9932	6.059
70	1.037	0.9913	7.669	0.850	0.9932	6.059
80	0.977	0.9913	7.669	0.801	0.9932	6.059
90	0.920	0.9863	11.229	0.755	0.9885	9.287
100	0.867	0.9863	11.229	0.712	0.9885	9.287
110	0.816	0.9863	11.229	0.670	0.9885	9.287
120	0.768	0.9863	11.229	0.631	0.9885	9.288
130	0.722	0.9863	11.229	0.594	0.9886	9.288
138	0.687	0.9863	11.229	—	—	—

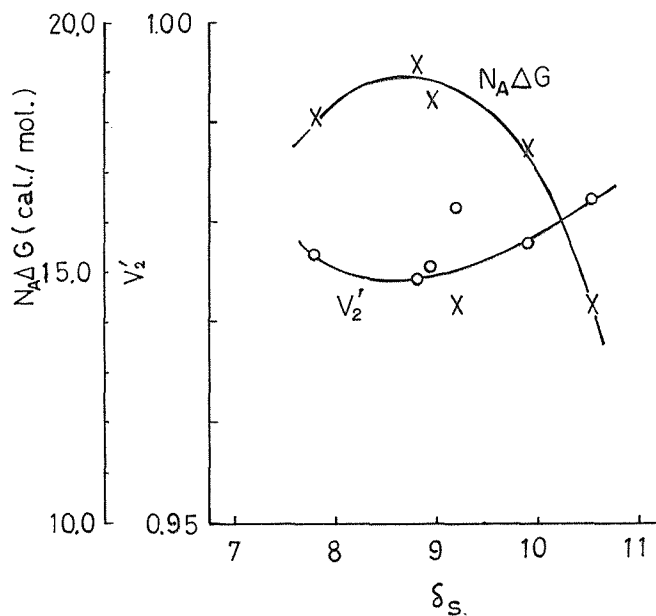


Fig. 3. $N_A\Delta G$ or v_2' plotted against solubility parameter of solvent, $\delta_s(\text{cal}/\text{cm}^3)^{1/2}$.

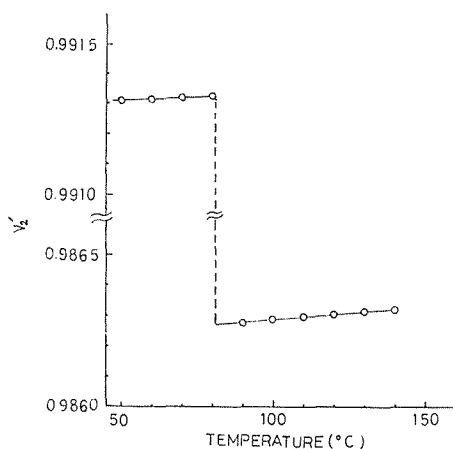


Fig. 4. v_2' plotted against temperature for polypropylene fiber in dibenzyl ether.

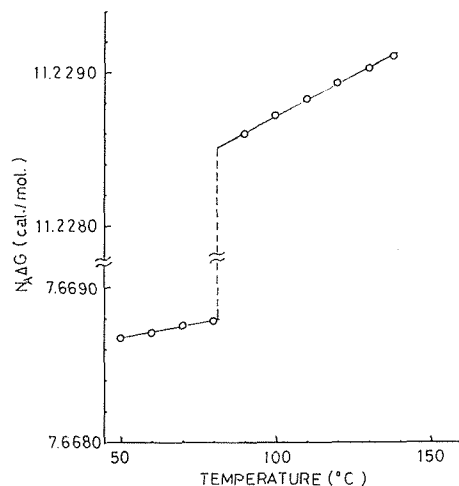


Fig. 5. $N_A \Delta G$ plotted against temperature for polypropylene fiber in dibenzyl ether.

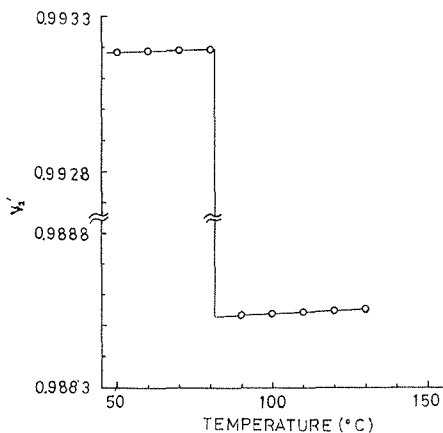


Fig. 6. v_2' plotted against temperature for polypropylene fiber in benzyl propionate.

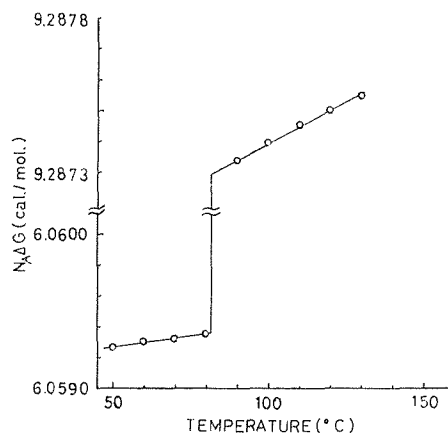


Fig. 7. $N_A \Delta G$ plotted against temperature for polypropylene fiber in benzyl propionate.

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